Parameter Optimization of Chemical Reduction of Graphene Oxide Using Design Expert

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***Abstract*— Graphene or also known as reduced graphene oxide exhibit variety of fascinating properties. Due to many possibilities to be utilized in wide field of application, the researches in fabrication had been made. Chemical reduction of graphene oxide is one of the methods known in synthesizing graphene. Graphene oxide was synthesized by the oxidation of graphite by following modified Hummer's method. In the reduction of graphene oxide, L-ascorbic was used as the reductant followed with addition of ammonia. This research was done optimize the reduction parameters (concentration of ascorbic acid, temperature and time of reduction reaction) to maximize the properties of reduced graphene oxide (rGO) using central composite design (CCD) from Design Expert® and to investigate the effect of chemical reduction of graphene oxide (GO) parameters towards the final properties of reduced graphene oxide (rGO) in term of phase composition, crystallinity, particle size and conductivity. The properties of rGO was characterized by undergoing different analysis which are crystalline structure analysis by XRD diffractometer, , zeta potential and particle size by Nano-ZS Zetasizer and finally the conductivity analysis by calculation of electrical conductivity of rGO suspension in deionized water. The optimum conditions of chemical reduction of GO are 17.612 mg/mL for the concentration of ascorbic acid, duration of 197.817 minutes at temperature 95 °C which predicted to result zeta potential of -16.70 mV in deionized water, has conductivity of 2.2 x10^{-2} S/m, particle size of 121.63 nm with interplanar spacing of 0.36 nm.**

***Keywords*— Ascorbic Acid, Central-Composite Design (CCD), Graphene Oxide (GO), Reduced Graphene Oxide (rGO).**

I. INTRODUCTION

Graphene or reduced graphene oxide (rGO) is a single-layer of carbon atom with sp2 hybridization tightly bonded with hexagonal-like structure. Graphene is known to be the lightest and thinnest substances known to man [5]. According to Geim [9], many researches were made to synthesis this allotrope of carbon because of its variety of fascinating properties. According to Kim, et al.[15] graphene exhibit transcendent thermal, mechanical and electrical properties as well as optical properties as it has transparency about 98% which is almost transparent. Due to its captivating properties, graphene has high potential to be applied in wide range of fields. According to the research made, graphene is known to be the best electrical conductor (high conductivity ~104 Ω^{-1} cm^{-1}) and the best heat conductor (thermal conductivity=5000$Wm^{-1}K^{-1}$) at ambient temperature and thus has high potential to be used as supercapacitors, composite compounds, sensors, electrodes and many other fields of applications [14].

Graphene was firstly produced accidentally using a scotch tape in 2004 by Geim, et al.[9] when Geim and Novoselov are trying to clean the graphite with scotch tape. Ever since graphene was introduced for its existence to the world, there are many methods has been used to synthesize graphene from graphite. Some of the methods known are mechanical exfoliation of graphite, epitaxial growth, chemical vapor deposition and finally, chemical reduction of graphene oxide (GO). Different methods will produce different properties of graphene. From all the methods mentioned, Hou, et al. [11] state that chemical reduction of graphene oxide (GO) is considered as advantageous since this methods known to be the fastest way to fabricate graphene as well as its cost effectiveness and bulk-scale productivity. This method involve two steps where graphene oxide is first produced before it chemically reduced to graphene. The first step involved the oxidation of graphite powder to form graphite oxide and continued with the second step where the graphite oxide is exfoliated to graphene oxide by ultrasonication. Several approach was done to prepare the graphene oxide such as Brodie method, Staudenmaier method, Hofmann method, Hummer's method and Tour method. In this study, modified Hummer's method is chosen due to the modification that had been made from the previous methods as this method is much safer and easier to perform than previous methods [2]. Another advantages of modified Hummer's (MH's) method is that adequate amount of graphene can be yielded and the graphene oxide produced is in the right quality in terms of number of sheets. According to Chua & Pumera [6], the alteration of graphene oxide to graphene can be observed by the change of the colour of the mixture from brown (graphene oxide) to black (graphene). Another change that can be observed is the increase of hydrophobicity.

In chemical reduction of graphene oxide, reductant was used to synthesize reduced graphene oxide (rGO). The reducing agents are divided into two categories that are 'well-supported' mechanisms and 'proposed' mechanisms. Well-supported mechanisms are comprises of traditionally applied reducing agents in synthetics chemistry and have shown explicit reaction modes to specific oxygen functional groups. While the proposed mechanisms is vice versa [6]. In this case, L-ascorbic acid or generally known as vitamin C is one type of reductant of proposed mechanisms. Basically, L-ascorbic acid was used as the reductant to reduce graphene oxide to graphene rather than using hydrazine, hydrazine hydrates or borohydrides as the reducing agents because this reducing agents is highly poisonous and explosive thus, L-ascorbic acid is used as the reducing agent due to its known properties where L-ascorbic acid has mild reductive ability, non-toxic and employed as a reductant in living organisms [25]. Alkaline condition with pH value ranging from 9 to 10 can yield more stable graphene and considered as favorable compare to neutral condition as alkaline condition promote colloidal stability of graphene oxide sheets through electrostatic repulsion and thus preventing agglomeration of graphene layers formed [8]. In order to achieve this condition, a specific amount of ammonia is added to the L-ascorbic acid until the pH value is between 9 to 10.

A central composite design (CCD) is the most commonly used response surface designed experiment. Central composite design is

a factorial or fractional factorial design with center points, augmented with a group of axial points (also called star points) that can estimate curvature. CCD can be used to efficiently estimate first- and second-order terms and model a response variable with curvature by adding center and axial points to a previously done factorial design. CCD was widely used statistical method based on the multivariate nonlinear model for the optimization of biosorption process variables and the regression model equations and operating conditions from the appropriate experiments were used. It is also interesting to study the interactions of the different parameters affecting the process [16].

Chemical reduction of graphene oxide is known as one of the method that widely used to synthesis graphene. Many reducing agents can be used for this process such as hydrazine, borohydride and ascorbic acid. In this study, ascorbic acid was selected as the reductant. Ammonia is usually added to the ascorbic acid to make sure the condition for the reduction process is in alkaline condition with pH range from 9-10. Some of the reduction parameters are need to be control for the reduction process to take place. For this research, the parameters are the concentration of ascorbic acid, the time of the reduction and the reduction temperature. Different concentration of ascorbic acid will synthesized reduced graphene oxide with different morphology and conductivity [12]. The duration of reduction process will affect the conductivity of the reduced graphene oxide synthesized [10] and the temperature will affect the optical and super capacitive properties of reduced graphene oxide [18]. These parameters must be controlled in order for the desired properties of reduced graphene oxide can be achieved which is the reduced graphene oxide will be used as sensor, thus the reduced graphene oxide should have great electrical conductivity as well as the optical and super capacitive properties. In this study, all three parameters that are ratio of ascorbic acid and ammonia, time of reduction and temperature of the reduction were optimized by using Central Composite Design (CCD) from Design Expert®. The concentration of ascorbic acid is in range of 0.05 mg/mL to 23.60 mg/mL, reduction time between 30 minutes to 312 minutes and temperature in range of 48 °C to 107 °C. The synthesized reduced graphene oxide is then characterized by XRD analysis, BET analysis, electrical conductivity, particle size and zeta potential analysis. The objectives of the study were to optimize the reduction parameters (concentration of ascorbic acid, temperature and time of reduction reaction) to maximize the properties of reduced graphene oxide (rGO) using central composite design (CCD) from Design Expert®, and to investigate the effect of chemical reduction of graphene oxide (GO) parameters towards the final properties of reduced graphene oxide (rGO) in term of phase composition, crystallinity, particle size and conductivity.

II. METHODOLOGY

A. Chemicals and Materials

Flake graphite powder (99% purity) was used as the source in synthesizing of GO. Hydrogen peroxide, H_2O_2 (with purity of 30%), hydrochloric acid, HCl (with purity 95-98%) and potassium permanganate, $KMnO_4$ were supplied by R&M Chemicals. L-ascorbic acid with purity of 99% and sulphuric acid, H_2SO_4 (98% purity) was obtained from Systerm Chemicals. Sodium nitrate, $NaNO_3$ with 99% purity (supplied by Systerm Chemicals) was used to enhance the rate of oxidation. Acetone (99% purity, supplied by Systerm Chemicals) was used to remove the moisture in GO, ammonia solution, NH_3OH (supplied by R&M Chemicals) was used to maintain the pH range from 9-10 of the reduction of GO and deionized water was used as washing solvent.

B. Preparations of GO

Graphene oxide (GO) was prepared using Modified Hummer's (MH's) method which is much safer and easier to perform than previous methods [2]. By referring to Junaidi et al. [13], 10 g of graphite powder (99.99% purity) was mixed with 5g sodium nitrate, NaNO3 (99.5% purity) and 400 mL of sulphuric acid, H2SO4 (95-98% purity) in a 2000 mL beaker. The mixture is maintain at low temperature under ice bath condition to make sure the temperature not exceeding 15 ℃ and stirred for 1 hour. 60 g of potassium permanganate (99-100% purity) was added quarterly within 2 hour to the mixture. The reaction is maintained at low temperature to avoid any gas involved during the oxidation and stirred for 20 hours.

Next, the step continued by heat up the mixture while being stirred to 70 ℃ and then 200 mL of deionized water was added slowly to the mixture for 1 hour and maintained for another 1 hour duration. After that, the mixture was heated again to 90 ℃ and another 200 mL of deionized water was added to the mixture slowly for 1 hour and kept under the same temperature for 1 hour duration. The heating of the mixture was stopped and 60 mL of hydrogen peroxide was added to stop the reaction. The mixture was kept at room temperature until no more bubbles is formed in the mixture. Two separated layers can be observed in the beaker, the bottom layer consist of suspended GO produced. The solution in the upper layer is then removed and the remained mixtures in the beaker is washed with dilute hydrochloric acid (HCl) solution (dilution factor of 160 HCl: 1840 deionized water) and deionized water twice for two days in a row. The pH of the mixtures was adjusted almost too neutral (pH 6 - pH 7) and centrifuged with 10 000 rpm for 20 mins at 20 ℃. The GO precipitate is then dried in an oven for 20 hours at 70 ℃ and washed with acetone to remove moisture that remains in the sample. Finally, the sample was dried again under the same temperature (70 ℃) for 20 hours in an oven.

C. Preparation of rGO

The chemical reduction of graphene oxide to reduced graphene oxide (rGO) was carried out by using L-ascorbic acid (vitamin C) as reducing agent [25]. The reduction is maintained under alkaline condition. According to Zainuddin, et al. [24], 1.5 g of GO is dissolved in 500 mL deionized water and stirred for 30 min. Next, the GO solution is sonicate for 2 hours and L-ascorbic acid is added slowly to the solution for 30 min. Ammonia solution is added to the mixture in order to achieve the alkaline condition with pH range between 9 to 10. After that, the mixture was stirred vigorously at specific temperature and duration. rGO formed is then washed with acetone and deionized water simultaneously and dried in oven for 24 hours at 60 to 70 ℃.

The entire step in synthesis of rGO carried out with several trial run with different parameters, which had been generated using Central Composite Design (CCD) from Design Expert®. Table 2 shows the trial run for the reduction of GO into rGO by varying the parameters required.

D. Experimental Design using Central Composite Design (CCD)

Response Surface Methodology (RSM) is a statistical and mathematical combination methodology used to select the optimum experimental conditions which require the lowest number of experiments in order to obtain the most appropriate results [3] [18]. A CCD with three independent variables was applied to determine the effect of concentration of ascorbic acid, reduction time and reduction temperature on the final properties of reduced graphene oxide (rGO) in term of phase composition, crystallinity, particle size and conductivity.

A total of 15 experiments were found to be sufficient to calculate the coefficients of the second order polynomial regression model for the variables. Each variables were scrutinized at five levels: -α, -1, 0, +1 and +α as shown in Table 1. The performance of the chemical

reduction of GO is explained by following the empirical second order polynomial model (equation (1)).

$$Y = X_0 + X_1A + X_2B + A_3C + X_{12}AB + X_{13}AC + X_{23}BC + X_{11}A^2 + X_{22}B^2 + X_{33}C^2 \quad (1)$$

Y is the characterization of the reduction of GO, X_0 is the interception coefficients, X_{11}, X_{22} and X_{33} are the quadratic terms, X_{12}, X_{13} and X_{23} are the interaction coefficient and A, B and C are the independent variables.

Data of the experiments were analyzed by analysis of variance (ANOVA), and p-value lower than 0.05 was considered significant in surface response analysis. Optimal values of the operation parameters were estimated by the three dimensional response surface analysis of the independent variables and the dependent variables.

Table 1: Optimization of parameters, experimental range and level of independent variables on chemical reduction of GO

	Range and Level				
Independent variable	-α	-1	0	+1	+α
Concentration of ascorbic acid (mg/mL)	5.94	0.05	8.83	17.61	11.73
Time of reduction (min)	100.39	30	135.00	240	169.61
Temperature of reduction (°C)	71.73	60	77.50	95	83.27

Table 2: Parameter of reduction of GO generated from CCD

Run	Parameter		
	Concentration of Ascorbic Acid (mg/mL)	**Time of Reduction (min)**	**Temperature of Reduction (°C)**
1	0.05	30	60
2	17.61	30	60
3	0.05	240	60
4	17.61	240	60
5	0.05	30	95
6	17.61	30	95
7	0.05	240	95
8	17.61	240	95
9	5.94	135	78
10	23.60	135	78
11	8.83	42	78
12	8.83	312	78
13	8.83	135	48
14	8.83	135	107
15	8.83	135	78

E. Characterization and Measurement

Fourier-Transformed Infrared Analysis (FTIR) - FTIR analysis was conducted to determine the chemical functional groups of graphite and GO after the synthesis process using Perkin Elmer Spectrum One.

X-ray Diffraction (XRD) Analysis - XRD patterns were obtained using a diffractometer (XRD, Philips Analytical, PW-3040) with CuKα as the radiation source with wavelength (λ = 0.15 nm). The XRD scan were carried out in a 2θ range from 10° to 90° with scanning rate of 2°/min using voltage of 40 kV and current of 40 mA.

Zeta Potential and Particle Size Analysis - Particle size and zeta potential analysis of both GO and rGO were performed using Nano-ZS Zetasizer (Malven, UK) in electronic scattering mode. 0.5 mg/mL of rGO suspensions in deionized water was prepared and sonicated for 10 minutes to form a homogenous solution.

Electrical Conductivity Analysis – The electrical conductivity analysis was done to measure the electrical conductivity of reduced graphene oxide synthesized. The analysis was performed by calculating the electrical conductivity of rGO suspension using Conductivity meter.

III. Results And Discussion

In this study, the synthesis of rGO was carried out by chemical reduction of GO by using ascorbic acid as the reducing agent in alkaline condition. The pH was maintained within range from 9-10 by adding ammonia solution to the GO mixture. According to Xu et al. [20], ascorbic acid deprotonated by forming dehydroascorbic acid and further converted into guluronic acid and oxalic acid. By adding ammonia solution to the mixture, the intermediate acids (dehydroascorbic acid) can be neutralized to prevent the accumulation of this acid products as well as to aid the reduction process. At the same time, the alkaline condition give electrostatic repulsion between rGO sheets [1] and hydrogen bonds are formed with the residual oxygen groups, including –COOH on the edge of GO sheets by the intermediates which inhibit the π-π stacking between rGO sheets and forbid the formation of aggregation, resulting stable rGO suspension. In simple words, GO is seen as the oxidant and ammonia solution as the stimulator to the process.

A. FTIR Analysis of GO and rGO

Before synthesizing rGO by following the reduction parameters in Table 1, GO formed was first analyzed using FTIR analysis in order to investigate the bonding interaction in the GO sample [22]. Fig. 1 shows the FTIR spectra of graphite and GO. From Fig. 1, the FTIR spectra of pure graphite shows no characteristic peaks for the distinguishable functional groups while in the FTIR spectrum of GO shows a broad peak at 3343 cm^{-1} which indicate the O-H hydroxyl stretching vibration, and three sharp peaks at 1721 cm^{-1}, 1620 cm^{-1}, 1145 cm^{-1} and 1036 cm^{-1} which indicates the C=O stretching (carbonyl group), aromatic C=C stretching vibration, epoxy C-O stretching vibration and stretching vibration of epoxy C-O groups respectively. Aunkor, et al. [3] prove it where the carbonyl group (C=O) in the peaks between 1700 – 1750 cm^{-1}, O-H stretching is in range of 2800 – 3500 cm^{-1}. The epoxy C-O stretching vibrations at range of 1000 – 1280 cm^{-1} and the aromatic C=C stretching vibration at peak 1616 cm^{-1} [10]. This indicates that the graphite is successfully oxidized into GO.

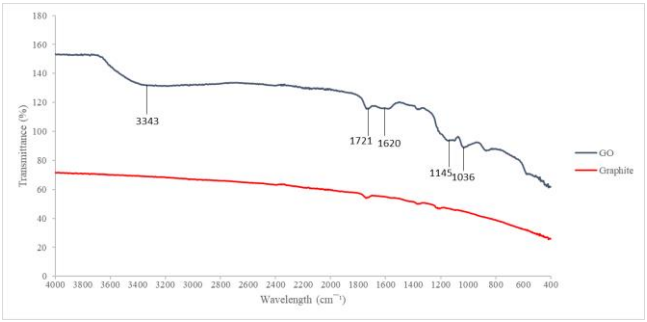

Fig. 1: FTIR spectra of graphite and GO.

B. Optimal Conditions

The performance of the chemical reduction of GO by using ascorbic acid as the reducing agent are depends on different parameters which are the concentration of reducing agent, duration of the reduction process and the temperature of the reaction. By defining the optimal levels of all variables require a large number of experiments. In order to simplify the analysis, the roles of each variables must be understood.

First, the characterization of rGO samples was conducted to study the effect of all three variables to the characteristics and composition of the rGO formed in terms of the crystalline structure, electrical conductivity, dispersion level of rGO in solution and the particle size of the rGO.

After the characterization of rGO has been performed, the data obtained was optimized using Design Expert software to predict the optimum value of the independent variables to maximize the characteristic of the rGO synthesized, which is almost the same to the characteristic of pristine graphene that suitable for the application of supercapacitor. A pristine graphene has high electrical conductivity value, smaller particle size, d-spacing ≈ 0.3 nm, and the zeta potential value is far from zero mV(isoelectric point).

C. XRD Analysis of rGO for CCD

XRD analysis of rGO was conducted to determine the interlayer spacing of rGO sheets in order to evaluate the structural information of the rGO samples[6]. The interlayer spacing (d-spacing) can be calculated by following to Bragg's Law [22]:

$$n\lambda = 2dsin\theta \quad (2)$$

Where n is the diffraction series, λ is the X-ray wavelength and θ is the diffraction angle. Fig. 2 shows the XRD patterns of rGO samples and Table 2 shows the interlayer spacing calculated at 2θ (22° to 26°). Different d-spacing values can be attributed to the various content of oxygen-containing groups between graphene layers [11]. From Fig. 2, the intense peak shows at some of the rGO samples st 2θ ≈ 10° (d-spacing ≈ 0.8 nm) indicates that the GO is not completely reduced to rGO. Completely reduced graphene oxide, rGO should exhibit high peak between 2θ = 20° to 25° [16] [17]. According to Liu, et al. [16], pristine graphite exhibit the basal reflection peaks at 2θ = 26.6° (d-spacing 0.335nm) which is quite similar with the peaks of rGO due to the deoxygenated functional group with differs in peak sharpness and particle size. It is observed that the intense peaks of all the rGO samples indicates the successfulness restoration of new graphitic network in rGO with different reduction reaction parameters.

Table 3: Interlayer spacing of rGO samples at 2θ

Sample	Degree, θ (°)	d- spacing (nm)
rGO(1)	22.95	0.385
rGO(2)	24.84	0.357
rGO(3)	24.94	0.356
rGO(4)	24.24	0.365
rGO(5)	24.51	0.362
rGO(6)	25.16	0.353
rGO(7)	24.19	0.366
rGO(8)	24.92	0.356
rGO(9)	24.92	0.356
rGO(10)	25.82	0.344
rGO(11)	25.14	0.353
rGO(12)	24.89	0.357
rGO(13)	24.80	0.358
rGO(14)	24.80	0.358
rGO(15)	24.53	0.361

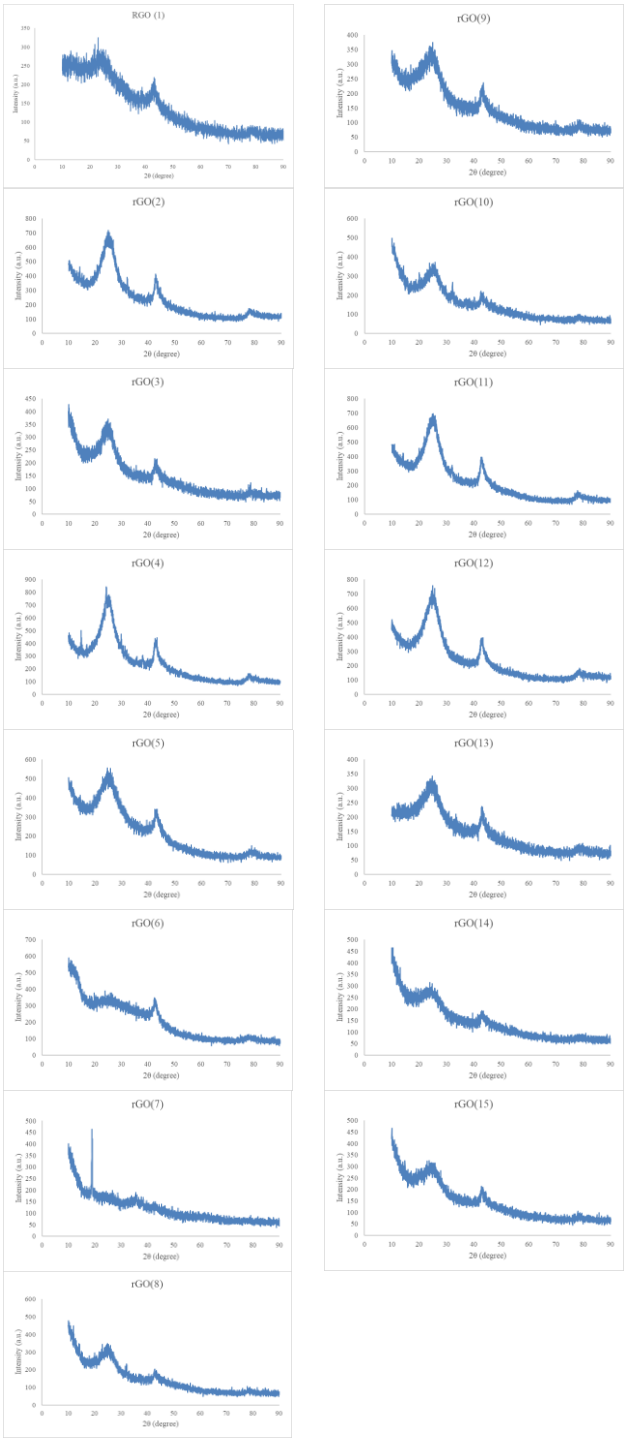

Fig. 2: XRD patterns of rGO

D. Zeta Potential and Particle Size Analysis for CCD

Dynamic light scattering zetasizer plays an important role to determine the zeta potential and particle size. Prior to testing, a solution 0.5 mg/ml rGO suspension in deionized water was prepared [22]. Deionized water is one of the best solvent to disperse rGO that remove hydrophobicity characteristic. The diameter particle sizes was in range between 28.37 nm to 1303 nm. While, the zeta potential value in range of -11.1mV to 27.2mV.

According to Tang, et al. [20], the isoelectric point (IEP) of rGO (zeta potential value of 0 mV) at pH ≈ 5. This indicate that rGO suspension near to 0 mV is easily agglomerate compare to rGO with zeta potential value far from the IEP. In this case, the rGO that has the most stable dispersion in deionized water is the rGO(14) with zeta potential value of -27.2 mV. The particle size and zeta potential value are shown in Table 4 below. The negative value of zeta potential indicate the rGO can disperse steadily at basic condition with pH more than pH 5.

Table 4: Zeta potential and particle size of rGO samples

Sample	Zeta Potential (mV)	Particle Size (nm)
rGO(1)	-15.90	1303.00
rGO(2)	-13.50	1264.00
rGO(3)	-18.00	807.40
rGO(4)	-11.90	716.20
rGO(5)	-14.20	735.70
rGO(6)	-12.10	323.60
rGO(7)	-16.10	106.30
rGO(8)	-15.50	49.59
rGO(9)	-11.10	829.10
rGO(10)	-11.80	408.00
rGO(11)	-17.00	28.37
rGO(12)	-15.90	379.80
rGO(13)	-16.90	370.80
rGO(14)	-27.20	425.20
rGO(15)	-11.30	343.80

E. Electrical Conductivity Analysis for CCD

RGO's electrical conductivity is the most important standards for assessing the degree of reduction and is governed by its structural properties. The conductivity improves in the present work by increasing the reduction time. This is due to the removal of the residual oxygen in the rGOs. Usually, reduced graphene oxide electrical conductivity was used to indicate the extent of electronic conjugation restored in deoxidizing GO [1]. Table 5 shows the conductivity values of each rGO samples. It is shown that the electrical conductivity of rGO was quite low. rGO(14) exhibits the highest conductivity (0.0247 S/m) and followed with rGO(10) with the value of 0.0231 S/m. the lowest conductivity is shown by rGO(12) with value of 0.015 S/m. According to Hanifah, et al. [10], GO is an electrically insulating material since most of the carbon atoms in GO are sp3 hybridized. The existence of many oxygen-containing functional groups breaks the conjugated structure and thus resulting in a decrease of carrier mobility and concentration. Incomplete reduction of graphene oxide may resulting low conductivity value of rGO.

Table 5: Electrical Conductivity of rGO Samples

Sample	Conductivity (S/m)
rGO(1)	0.019
rGO(2)	0.016
rGO(3)	0.019
rGO(4)	0.015
rGO(5)	0.017
rGO(6)	0.019
rGO(7)	0.017
rGO(8)	0.019
rGO(9)	0.017
rGO(10)	0.023
rGO(11)	0.016
rGO(12)	0.015
rGO(13)	0.015
rGO(14)	0.025
rGO(15)	0.018

F. RSM Model Development

In this study, the effect of all three factors on the reduction of GO including the concentration of ascorbic acid, time of reduction and temperature of reduction were selected as the factors in CCD. As the responses, the d-spacing, electrical conductivity, zeta potential and particle size are selected. With total number of 15 experiments implemented for the response surface modelling and the order of the experiments were arranged randomly. The observed results are shown in Table 6.

Table 6: Experimental designs arrangement and experimental results

Run number	A	B	C	Response			
				Zeta potential (mV)	Conductivity (S/m)	Particle size (nm)	d-spacing (nm)
1	0.05	30	60	-15.90	0.019	1303.00	0.385
2	17.61	30	60	-13.50	0.016	1264.00	0.357
3	0.05	240	60	-18.00	0.019	807.40	0.356
4	17.61	240	60	-11.90	0.015	716.20	0.365
5	0.05	30	95	-14.20	0.017	735.70	0.362
6	17.61	30	95	-12.10	0.019	323.60	0.353
7	0.05	240	95	-16.10	0.017	106.30	0.366
8	17.61	240	95	-15.50	0.019	49.59	0.356
9	5.93	135	77.5	-11.10	0.017	829.10	0.356
10	23.6	135	77.5	-11.80	0.023	408.00	0.344
11	8.83	42	77.5	-17.00	0.016	28.37	0.353
12	8.83	312	77.5	-15.90	0.015	379.80	0.357
13	8.83	135	48	-16.90	0.015	370.80	0.358
14	8.83	135	107	-27.20	0.025	425.20	0.358
15	8.83	135	77.5	-11.30	0.018	343.80	0.361

The model suitability was tested using the ANOVA test. Therefore, the second-order polynomial equation are expressed by:

Final equation in term of Zeta potential,

$$Y = X_0 + X_1A + X_2B + A_3C + X_{12}AB + X_{13}AC + X_{23}BC + X_{11}A^2 + X_{22}B^2 + X_{33}C^2 \quad (2)$$

Where, X_{ij} is the polynomial equation coefficient (constant) for the Zeta potential response, the value of X_{ij} are:

X_0	-12.8500
X_1	+0.8364
X_2	-0.4756
X_3	-1.1700
X_{12}	+0.2750
X_{13}	-0.7250
X_{23}	-0.6000
X_{11}	+0.6866
X_{22}	-0.4237
X_{33}	-2.8500

Final equation in term of conductivity

$$Y = X_0 + X_1A + X_2B + A_3C + X_{12}AB + X_{13}AC + X_{23}BC + X_{11}A^2 + X_{22}B^2 + X_{33}C^2 \quad (3)$$

Where, X_{ij} is the polynomial equation coefficient (constant) for the conductivity response, the value of X_{ij} are:

X_0	+0.0173
X_1	$+3.586 \times 10^{-06}$
X_2	+0.0003
X_3	+0.0014
X_{12}	-0.0001
X_{13}	+0.0015
X_{23}	-0.0001
X_{11}	+0.0015
X_{22}	-0.0014
X_{33}	+0.0007

Final equation in term of particle size

$$Y = X_0 + X_1A + X_2B + A_3C + X_{12}AB + X_{13}AC + X_{23}BC + X_{11}A^2 + X_{22}B^2 + X_{33}C^2 \quad (4)$$

Where, X_{ij} is the polynomial equation coefficient (constant) for the particle size response, the value of X_{ij} are:

X_0	+343.0700
X_1	-119.6700
X_2	-174.1100
X_3	-203.4400
X_{12}	+37.9000
X_{13}	-42.3300
X_{23}	+17.5000
X_{11}	+139.5300
X_{22}	+102.1000
X_{33}	+38.9400

Final equation in term of d-spacing

$$Y = X_0 + X_1A + X_2B + A_3C + X_{12}AB + X_{13}AC + X_{23}BC + X_{11}A^2 + X_{22}B^2 + X_{33}C^2 \quad (5)$$

Where, X_{ij} is the polynomial equation coefficient (constant) for the d-spacing response, the value of X_{ij} are:

X_0	+0.3552
X_1	-0.0056
X_2	-0.0017
X_3	-0.0019
X_{12}	+0.0045
X_{13}	-0.0001
X_{23}	+0.0036
X_{11}	+0.0012
X_{22}	+0.0026
X_{33}	+0.0017

G.Statistical Analysis

Table 7 to 10 shows the results of analysis of variance (ANOVA). The results are summarized to the test the soundness of the model. ANOVA is a statistical method that subdivides the total variation in a set of data into component parts associated with specific sources of variation for the purpose of evaluating hypotheses on the parameters of the model [18]. The mean square value were calculated by dividing the sum squares of each variation source by degree of freedom and 95% confidence level ($\alpha = 0.05$) was used to determine the statistical significance in all analyses.

i Response 1: Zeta Potential

The Model F-value of 1.05 implies the model is not significant relative to the noise. There is a 50.86% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case, there are no significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. A negative Predicted R^2 implies that the overall mean may be a better predictor of the response than the current model. In some cases, a higher order model may also predict better.

Table 7: ANOVA for the response (zeta potential) quadratic model

Sources	Sum of squares	Degree of freedom	Mean squares	f-value	p-value	Remarks
Model	148.79	9	16.53	1.05	0.51	not significant
A-Concentration of AA	6.24	1	6.24	0.39	0.56	-
B-Time of reduction	2.25	1	2.25	0.14	0.73	-
C-Temperature	18.62	1	18.62	1.18	0.33	-
AB	0.61	1	0.60	0.04	0.85	-
AC	4.20	1	4.20	0.27	0.63	-
BC	2.88	1	2.88	0.18	0.69	-
A^2	3.06	1	3.06	0.19	0.68	-
B^2	1.07	1	1.07	0.07	0.80	-
C^2	82.36	1	82.36	5.21	0.07	-
Residual	79.02	5	15.80	-	-	-
Cor. Total	227.81	14	-	-	-	-
-	R^2 = 0.6531	R^2_{adj} = 0.0287	$R^2_{predicted}$= -2.5148	-	-	-

ii Response 2: Conductivity

The Model F-value of 1.74 implies the model is not significant relative to the noise. There is a 28.17% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case, there are no significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. A negative Predicted R^2 implies that the overall mean may be a better predictor of the response than the current model. In some cases, a higher order model may also predict better.

Table 8: ANOVA for the response (conductivity) quadratic model

Sources	Sum of squares	Degree of freedom	Mean squares	f-value	p-value	Remarks
Model	0.0001	9	9.60×10^{-06}	1.7400	0.2817	not significant
A-Concentration of AA	1.15×10^{-10}	1	1.15×10^{-10}	0.0000	0.9965	-
B-Time of reduction	7.99×10^{-07}	1	7.99×10^{-07}	0.1400	0.7194	-
C-Temperature	0.0000	1	0.0000	5.0900	0.0737	-
AB	4.50×10^{-08}	1	4.50×10^{-08}	0.0081	0.9316	-
AC	0.0000	1	0.0000	3.1500	0.1361	-
BC	8.00×10^{-08}	1	8.00×10^{-08}	0.0145	0.9089	-
A^2	0.0000	1	0.0000	2.7700	0.1571	-
B^2	0.0000	1	0.0000	2.2500	0.1939	-
C^2	4.68×10^{-06}	1	4.68×10^{-06}	0.8468	0.3997	-
Residual	0.0000	5	5.53×10^{-06}	-	-	-
Cor. Total	0.0001	14	-	-	-	-
-	R^2 = 0.7577	R^2_{adj} = 0.3215	$R^2_{predicted}$= -2.0521	-	-	-

iii Response 3: Particle Size

The Model F-value of 0.58 implies the model is not significant relative to the noise. There is a 77.24% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case, there are no significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. A negative Predicted R^2 implies that the overall mean may be a better predictor of the response than the current model. In some cases, a higher order model may also predict better.

Table 9: ANOVA for the response (particle size) quadratic model

Sources	Sum of squares	Degree of freedom	Mean squares	f-value	p-value	Remarks
Model	$1.12 \times 10^{+06}$	9	$1.25 \times 10^{+05}$	0.5841	0.7724	not significant
A-Concentration of AA	$1.28 \times 10^{+05}$	1	$1.28 \times 10^{+05}$	0.5978	0.4744	-
B-Time of reduction	$3.01 \times 10^{+05}$	1	$3.01 \times 10^{+05}$	1.4100	0.2883	-
C-Temperature	$5.66 \times 10^{+05}$	1	$5.66 \times 10^{+05}$	2.6500	0.1644	-
AB	11490.52	1	11490.52	0.0538	0.8258	-
AC	14332.09	1	14332.09	0.0671	0.8060	-
BC	2449.65	1	2449.65	0.0115	0.9189	-
A^2	$1.26 \times 10^{+05}$	1	$1.26 \times 10^{+05}$	0.5912	0.4767	-
B^2	62328.31	1	62328.31	0.2917	0.6123	-
C^2	15399.45	1	15399.45	0.0721	0.7991	-
Residual	$1.07 \times 10^{+06}$	5	$2.14 \times 10^{+05}$	-	-	-
Cor. Total	$2.19 \times 10^{+06}$	14	-	-	-	-
-	$R^2 = 0.5125$	$R^2_{adj} = -0.3650$	$R^2_{predicted} = -3.1291$	-	-	-

iv Response 4: d-spacing

The Model F-value of 1.08 implies the model is not significant relative to the noise. There is a 49.21% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case, there are no significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. A negative Predicted R^2 implies that the overall mean may be a better predictor of the response than the current model. In some cases, a higher order model may also predict better.

Table 10: ANOVA for the response (d-spacing) quadratic model

Sources	Sum of squares	Degree of freedom	Mean squares	f-value	p-value	Remarks
Model	0.0007	9	0.0001	1.0800	0.4921	not significant
A-Concentration of AA	0.0003	1	0.0003	3.7300	0.1113	-
B-Time of reduction	0.0000	1	0.0000	0.3734	0.5679	-
C-Temperature	0.0001	1	0.0001	0.6982	0.4415	-
AB	0.0002	1	0.0002	2.1600	0.2013	-
AC	8.00×10^{-08}	1	8.00×10^{-08}	0.0011	0.9751	-
BC	0.0001	1	0.0001	1.3600	0.2959	-
A^2	9.06×10^{-06}	1	9.06×10^{-06}	0.1223	0.7408	-
B^2	0.0000	1	0.0000	0.5410	0.4951	-
C^2	0.0000	1	0.0000	0.3878	0.5608	-
Residual	0.0004	5	0.0001	-	-	-
Cor Total	0.0011	14	-	-	-	-
-	$R^2 = 0.6608$	$R^2_{adj} = 0.0503$	$R^2_{predicted} = -3.7052$	-	-	-

H.Effects of Model Parameters and Their Interactions

The significance of each model parameter was determined by means of Fischer's f-value and p-value. The f-value is the test for comparing the curvature variance with residual variance and probability >F (p-value) is the probability of seeing the observed f-value if the null hypothesis is true. Small probability values call for rejection of the null hypothesis and the curvature is not significant. Therefore, the larger the value of f and smaller p-value, the more significant the corresponding coefficient is.

3D surfaces is the graphical representation of the regression equation for the optimization of the conditions of reaction and are the most useful approach in revealing the conditions of the reaction system. In such plots, the responses functions of two factors are presented while the other one factor at fixed levels. The results of the interactions between three independent variables and dependent variables are shown in Fig 3 to Fig 6.

i Response 1: Zeta Potential

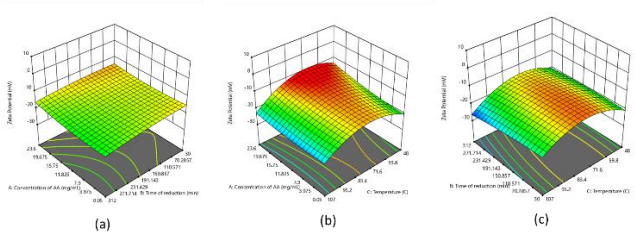

Fig. 3: Effect of concentration of ascorbic acid, time of reduction and temperature of reduction on Zeta potential value of chemical reduction of GO. (a) temperature was kept constant at 93.6 °C; (b) reduction time kept constant at 221.1 min; (c) concentration of ascorbic acid was kept constant at 3.738 mg/mL

ii Response 2: Conductivity

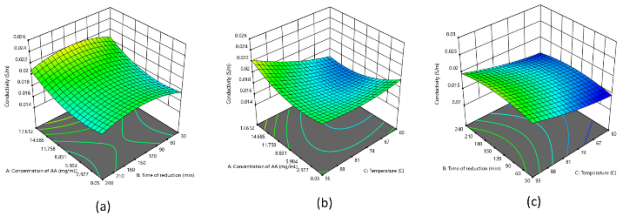

Fig. 4: Effect of concentration of ascorbic acid, time of reduction and temperature of reduction on conductivity of chemical reduction of GO. (a) temperature was kept constant at 93.95 °C; (b) reduction time kept constant at 166.5 min; (c) concentration of ascorbic acid was kept constant at 14.627 mg/mL

iii Response 3: Particle Size

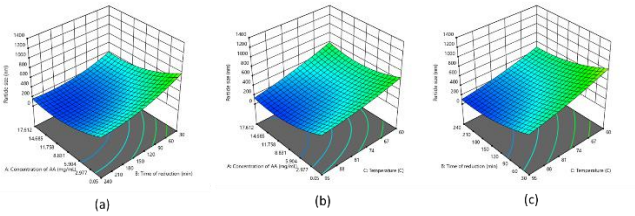

Fig. 5: Effect of concentration of ascorbic acid, time of reduction and temperature of reduction on particle size of rGO. (a) temperature was kept constant at 92.55 °C; (b) reduction time kept constant at 237.9 min; (c) concentration of ascorbic acid was kept constant at 10.412 mg/mL

iv Response 4: d-spacing

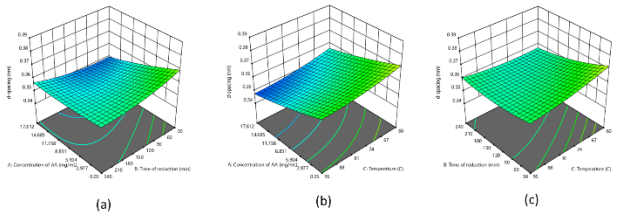

Fig. 6: Effect of concentration of ascorbic acid, time of reduction and temperature of reduction on d-spacing of rGO. (a) temperature was kept constant at 81.35 °C; (b) reduction time kept constant at 69.9 min; (c) concentration of ascorbic acid was kept constant at 3.914 mg/mL

I. Prediction of the Optimum Condition of Chemical Reduction of GO

To confirm the model's adequacy for predicting the optimum responses, a new experiment can be carried out using the optimum levels, as shown in Table 11. The results from Table 11 predicted that with the predicted values of the factors of the chemical reduction of GO, the optimum results with desirability of 61.5 % can be achieved.

Table 11: Optimum value of the parameter for the chemical reduction of GO and the predictive result.

Parameter	Optimum value	Predicted value of response			
		Zeta potential (mV)	Conductivity (S/m)	Particle size (nm)	d-spacing (nm)
A (Ascorbic acid, mg/mL)	17.612	-16.70	0.03	121.63	0.36
B (time, min)	197.817				
C (temp, °C)	95				

IV. CONCLUSION

In this research, it is found that the GO is successfully synthesized from graphite by following the MH's method. This finding can be confirmed by the FTIR spectra of both graphite and GO where the peaks observed indicate the hydroxyl (O-H) stretching vibration, carbonyl group (C=O) stretching, O-H deformation and epoxy (C-O) stretching vibration in GO sample, compare to graphite where it shows no characteristic peaks for the distinguishable functional groups. The optimal condition of the chemical reduction of GO are determined by using the RSM based on CCD. It can be conclude that combination of RSM based on CCD proved to be a powerful tools in optimization of chemical reduction of GO. The optimal condition for the reduction are 17.612 mg/mL for the concentration of ascorbic acid, duration of 197.817 minutes at temperature 95 °C. By using these optimized value, the chemical reduction predicted could resulting rGO with zeta potential of -16.6981 mV in deionized water, has conductivity of 2.2 x10^{-2} S/m, particle size of 121.625 nm with interplanar spacing of 0.355 nm.

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